Indian J. Phys. **75A** (1), 73-75 (2001)

IJP A
— an international journal

Electronic properties and compound formation in LiPb molten alloys

A K Rukhaiyar[1], V N Singh[2], A K Mishra[3], and R N Singh[4]*

[1]Department of Physics, S. K. M. College, Begusarai-851 101, Bihar, India
[2]Department of Physics, S. B. S. S. P. S. J. College, Patharganna, Godda-, India
[3]Department of Physics, Sabour College, Sabour-813 210, India
[4]Department of Physics, R. N. Lall College, Lakhisarai, India

Abstract : Concept of complex formation has been incorporated in the structure of Faber- Ziman formula to determine the electrical resistivities of liquid metal alloys which exhibit large deviation from metallic behaviour around specific compositions. This has then been applied to account for the anomalous electrical behaviour of liquid LiPb alloys

The study reveals that the anomalous electrical behaviour of liquid LiPb occurs due to preferential ordering of unlike atoms Theoretical study suggests that the intermetallic compound LiPb exists at concentration $C_{Li} = 0.8$. Our theoretical computation has been found to be successful in explaining the asymmetric behaviour of thermodynamic, microscopic and electronic properties such as free energy of mixing, partial structure factor and electrical resistivities

Keywords · Complex formation, structure factor, pseudomolecules

PACS Nos. 61 25.Mv, 83 70 Hq, 64 75 +g

1. Introduction

The asymmetric behaviour of mixing may be attributed to strong interactions [1, 2] for those binary alloys in which size effect is not large enough to be the cause of anomaly. Large excess free energy of mixing, heat of mixing, entropy of mixing are the characteristics [3-5] of the compound forming alloys. Various theoretical models [6-8] based on the formation of complexes have been used to investigate alloying behaviour of such types of binary molten alloys.

The concentration dependent electric [9] and thermodynamic [10] properties deviate maximally from the ideal values around concentrations close to the configuration Li_4Pb. Hoshino and Young [11] have used the hard sphere model to compute the entropy of mixing and a qualitative explanation of resistivity was obtained by them [12] with a model in which formation of complex is assumed. This model has successfully explained the thermodynamic properties of a number of compound forming alloys [13] and to some extent the electrical resistivity [14]. In this model, the existence of preferential association among the constituent species *i.e.*, $\mu A + \nu B \leftrightarrows A\mu B\nu$ (μ, ν are small integers) in the liquid state is considered.

* Corresponding Author

In the present work, the Faber- Ziman formula [15] of electrical resistivity for binary liquid alloys has been improved in the light of the complex formation model. Here correlations between the free ions, of pseudomolecules with free ions and between pseudomolecules are evaluated for the hard sphere reference system following the work of Hoshino [16].

2. Complex formation model

Let a liquid binary alloy containing in all $N_A = (1-C)N$ atoms of A and $N_B = CN$ atoms of B be assumed to consist of n_1N free atoms A, n_2N free atoms B and n_3N complexes $A\mu B\nu$ which also act as independent scattering centres in the alloy. Therefore from the conservation of atoms,

$$n_1 = 1 - C - \mu n_3,$$
$$n_2 = C - \nu n_3,$$
$$n = n_1 + n_2 + n_3. \quad (1)$$

Here, C is the concentration of the second species B. The volume in which free atoms are randomly distributed can be expressed as

$$\Omega = \Omega_{alloy} - n_3 N V_c, \quad (2)$$

where Ω_{alloy} is the volume of the alloy and V_c the volume of the complex

$$V_c = \mu\Omega_1 + \nu\Omega_2, \tag{3}$$

Ω_1, Ω_2 are the atomic volumes of the first and second species of the alloy, respectively. The number of complexes n_3 is obtained through the condition

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0. \tag{4}$$

The conformal solution approximation [17] enables us to express the free energy of mixing G_M as

$$G_M = -n_3 g + RT\sum_{i=1}^{3} n_i (\ln n_i - \ln n) + \sum\sum_{i<j} \frac{n_i n_j}{n} W_{ij}. \tag{5}$$

First term $(-n_3 g)$ lowers the free energy of the alloy due to formation of chemical complexes and W_{ij} $(i, j = 1, 2, 3)$ are the interaction energies. g is the free energy per molecule of the complex.

3. Electrical resistivity

The Faber-Ziman formula [15] has been extended to calculate the electrical resistivity of ternary mixture as

$$R = \frac{3\pi}{he^2}\frac{4\Omega_1}{V_F^2}\int_0^1 d(q/2K_F)(q/2K_F)^3$$

$$\sum_{i<j}^{1,2,3}\left(X_i V_i^2(q) S_{ii}(q) + 2(X_i X_j)^{1/2} V_i(q) V_j(q) S_{ij}(q)\right). \tag{6}$$

Here, V_F is the Fermi velocity of the phonon wave vector, $\Omega_1 = \Omega/n$ is the scattering volume of the alloy in which the free electrons travel, $V_i(q)(i = 1,2) = W_i(q)/\epsilon^*(q)$ are the screened form factors of Li and Pb and $V_3(q) = (\mu V_1(q) + \nu V_2(q))/(\mu + \nu)$ is the screened form factor of the complex, $\epsilon^*(q)$ is the modified Hartree dielectric function. The compute unscreened form factors, $W_i(q)$, the Heine–Abarenkov model potential has been considered. $S_{ij}(q)$ are the partial structure factors which have been obtained following the work of Hoshino [16]. The hard sphere diameters σ_1, σ_2 needed to compute $S_{ij}(q)$ have been determined as a function of concentration by minimizing the interionic pair potential

$$\theta(\sigma_i) = \theta_{min} + \tfrac{3}{2} K_B T. \tag{7}$$

Here, $\tfrac{3}{2} K_B T$ is the mean Kinetic energy and θ_{min} the depth of the first minimum in the interionic pair potential, which for binary alloy may be given as

$$\theta_{ij}(i, j = 1,2) = \frac{Z_i Z_j e^2}{R}\left[1 + \frac{\Omega}{\pi^2 Z_i Z_j}\int_0^\infty F_{ij}\frac{q^2 Sin(qR)}{qR}\,dq\right] \tag{8}$$

where Z_i, Z_j are the valencies of the constituent elements and e the electronic charge. F_{ij} in the local approximation is expressed as

$$F_{ij} = -\left(\frac{\Omega q^2}{8\pi} W_i(q) W_j(q) \frac{\epsilon^*(q) - 1}{\epsilon^*(q)} \frac{1}{1 - G(q)}\right). \tag{9}$$

$G(q)$ takes into account the effect of exchange and correlation among the conduction electrons and Vashishta and Singwi [18] form has been considered here. The Fermi wave vector needed to compute the unscreened form factors is obtained as

$$K_F = \left(\frac{3\pi^2\{(1-C)Z_i + CZ_j - 2n_3\}}{\Omega_{alloy} - n_3 N V_c}\right)^{1/3}. \tag{10}$$

Ω_{alloy} for LiPb has been taken from Ruppersberg and Speicher [19]. θ_{ij} has been calculated for the full range of concentration and values of σ are determined through [4] for Li and Pb.

4. Results and discussion

The equilibrium values of n_3 have been obtained through eqs. (4) and (5) and for this only one particular value for each interaction energy g and W_{ij} (g/RT = 13.215, W_{12}/RT = – 8.0, W_{13}/RT = – 5.455, W_{23}/RT = – 5.5) for the whole concentration range has been chosen which predicts Gibb's free energy of mixing G_M. The values of n_3 thus obtained and the computed free energy of mixing are shown in Figure 1 along with the experimental values [10]. The figure shows that the calculated values of G_M agree well with the experimental values.

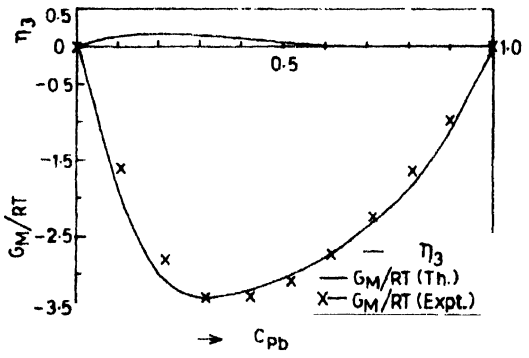

Figure 1. Upper side – n_3, Lower side – GM/RT *versus* concentration of Pb (C_{Pb}).

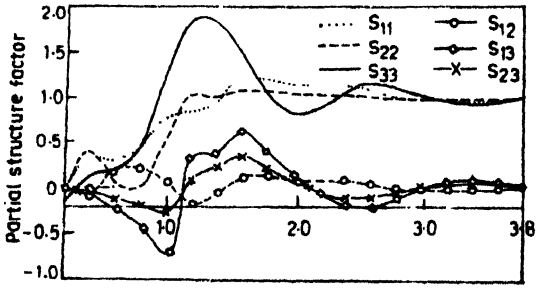

Figure 2. Partial structure factors *versus* wave vector (q).

The partial structure factors are computed following the work of Hoshino [16] and are shown in Figure 2. S_{11}, S_{22} remain positive whereas the values of S_{12}, S_{13}, S_{23} may be both positive and negative. S_{33} is negative upto q = 0.3 and after that it becomes positive. The hard sphere diameters σ_1 and σ_2 needed to compute $S_{ij}(q)$ have been obtained through eq. (7) and the diameter of Complex σ_3, has been considered as parameter which is taken here as 0.4544 nm.

The electrical resistivity of LiPb liquid alloys has been computed using eq. (6) and is shown in Figure 3 along with the experimental [9] values. R_1 is the contribution due to scattering from bare ions and R_2 that from the complexes. It is found that R_2 is maximal around the stoichiometric compositions and falls quickly to zero as the percentage of Pb increases. In Pb rich end of the contribution comes from the bare ion scattering R_1. Both R_1 and R_2 add together to give a pronounced peak in the electrical resistivity near $C_{pb} = 0.2$. The computed and experimental values are in reasonable agreement.

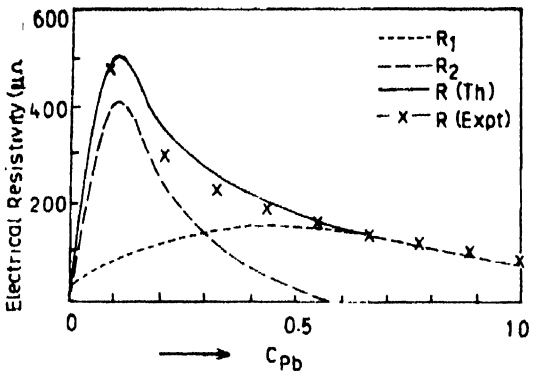

Figure 3. Electrical resistivity versus concentration of Pb (C_{Pb})

5. Conclusion

The constituent species in LiPb are simple s-p bonded metals. The size factor $(\Omega_{Pb} / \Omega_{Li}) = 1.38$ is a small number to bring asymmetry. The electronegativity (EN = 1-exp(−0.25 χ^2), χ is the difference in EN values of two metals) value of 0.086 for LiPb yields a weaker ionic character as compared to 0.51 for the well known ionic system CsAu [20]. It is believed that the constituent metals of such liquid alloys undergo major structural changes in atomic and electronic character after alloying. We state that preferential ordering of unlike atoms as nearest neighbours brings the concentration dependent anomaly.

Acknowledgment

The authors are thankful to Dr. R. N. Singh, Professor of Physics, S.Q. University, Oman for encouragement and Dr. B. B. Sahay, Professor of Physics, BCE, Bhagalpur for useful discussion. Financial assistance from the Council of Scientific & Industrial Research is acknowledge by Dr. A. K. Mishra.

References

[1] W H Young *Rep Prog Phys* **55** 1769 (1992)
[2] R N Singh and N H March *Intermetallic compounds*, **Vol 1-Principles** ed J H West brook, R L Fischer (New York Wiley) **661** (1994)
[3] A K Mishra, R N Singh and B B Sahay *Physica* **B167** 7 (1990)
[4] A K Mishra, R N Singh, R K Rukhaiyar and B B Sahay *Phy Stat Sol. (a)* **144** 335 (1994)
[5] L C Prasad, S K Chatterjee and V N Singh *Physica* **B217** 285 (1996)
[6] R N Singh and F Sommer *Rep Prog Phys.* **60** 51 (1997)
[7] L C Prasad, R N Singh, G P Singh and V N Singh *J Phys Chem (Am. Chem Soc.)* **102** 921 (1998)
[8] H Khan and K S Sharma *Indian J Pure Appl Phys* **36** 532 (1998)
[9] V T Nguyen and J E Enderby *Phil Mag* **35** 1013 (1977)
[10] M L Saboungi, J Marr and M Blander *J Chem Phys.* **68** 1375 (1978)
[11] K Hoshino and W H Young *J. Phys.* **F10** 1365 (1980)
[12] K Hoshino and W H Young *J Phys* **F10** L193 (1980)
[13] H M Michael and B B Sahay *Phys Stat Sol(b)* **178** 295 (1993)
[14] A K Mishra and B B Sahay *Phys Stat Sol (b)* **164** 267 (1991)
[15] T E Faber and J M Ziman *Phil. Mag* **11** 153 (1965)
[16] K Hoshino *J Phys* **F13** 1981 (1983)
[17] H C Longuet-Higgins *Proc. Roy. Soc* **A205** 247 (1951)
[18] P Vashishta and K S Singwi *Phys Rev* **B6** 875 (1972)
[19] H Rupersberg and W Speichet *Z Naturforsch* **A31** 47 (1976)
[20] F Hensel *Adv Phys.* **28** 555 (1979)